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Cincinnati, Ohio

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ABSTRACT

A comparative study was made of the ability of aluminum chlorohydrate to remove phosphate from wastewater. Removal of phosphate is important in many situations to prevent the nutrient enrichment of receiving waters with corresponding stimulation of algal growth.

The cost of the chemical for removing phosphates is an important consideration. In aluminum chlorohydrate, not all of the hydroxyls of alumina are replaced by chloride. Consequently it is potentially a cheaper chemical than aluminum chloride or even aluminum sulfate. The primary objective of this study was to determine the effect of the proportion of chloride in the chlorohydrate on its ability to remove phosphate.

The results of this work show that phosphate removal is poor when the proportion of hydroxyl in the aluminum chlorohydrate is high. Increasing the chloride content increases the effectiveness of phosphate removal. A complex polyion structure is indicated, in which most of the aluminum atoms are shielded from the solution. Increasing the proportion of chloride to hydroxyl reduces the size of the polyion, making more aluminum atoms available for phosphate removal.

Aluminum sulfate removed phosphate more effectively than chlorohydrate containing a high hydroxyl content. This difference was reduced by increasing the chloride content of the chlorohydrate. It is interesting to note that the high hydroxyl chlorohydrates were at least as effective in conditioning sludges for filtration as aluminum sulfate.

Key words: phosphorus removal, nutrients, aluminum chlorohydrate, aluminum sulfate

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SUMMARY

Aluminum chlorohydrate, approximately $Al_2(OH)_4Cl_2$, is currently used in Great Britain as a conditioning agent for wastewater treatment sludges to aid filtration. In this paper a comparative study between the ability of aluminum chlorohydrate and aluminum sulfate to remove phosphorus from wastewater was made. We have found that aluminum chlorohydrate is not a good precipitant for phosphates in wastewater. The product has been synthesized in the laboratory and found to behave as a complex polyion in which most of the aluminum atoms are shielded from the other ions in solution. Additional results show that treatment of aluminum chlorohydrate with hydrochloric acid increases the effectiveness of phosphate removal. Aluminum sulfate removed phosphate more effectively than aluminum chlorohydrate containing a high hydroxyl content. Sludge conditioning results showed that aluminum chlorohydrates are at least as effective as aluminum sulfate for conditioning prior to filtration.

INTRODUCTION

Phosphates present in wastewaters have recently become an important factor in the abatement of water pollution. With the advent of modern detergents, in which phosphates are present, our surface waters are receiving appreciable amounts of phosphate, promoting algal growth. This growth in turn leads to accelerated eutrophication and reduces the

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value of the water. Conditioning the wastewater with chemicals to reduce phosphates is one way of helping to prevent polluted waters. Chemicals such as ferric chloride, alum, and lime, alone or in combination with synthetic polymers,[1] have been used in a variety of ways to coagulate and remove phosphates from sewage.

Many of the chemicals used to remove phosphates are also effective in conditioning sludges prior to vacuum filtration. Superficially, at least, there appears to be a relationship between the ability to remove phosphate and the ability to condition sludge for dewatering. Aluminum chlorohydrate is a chemical which has been used in Europe,[2,3] as a sludge conditioner. Consequently, there appeared to be a justification for investigating its potential for phosphate removal.

Aluminum chlorohydrate may have different degrees of "basicity"[4] as represented by the following equations:

$$\underset{\text{67\% basicity}}{2Al(OH)_3} + 2HCl \longrightarrow Al_2(OH)_4Cl_2 + H_2O \quad (1)$$

$$\underset{\text{83\% basicity}}{2Al(OH)_3} + HCl \longrightarrow Al_2(OH)_5Cl + H_2O \quad (2)$$

The term "basicity" refers to the fraction of hydroxyl groups in the original aluminum hydroxide which have not been replaced.

Aluminum chlorohydrate, if effective for phosphate removal, would have some advantages over aluminum containing chemicals such as aluminum sulfate. Its acidity is much lower, so it would cause a lower pH drop. This could be important in water of low alkalinity. The chloride ion is less objectionable than sulfate in water and, for a given aluminum dosage, the amount of anion introduced would be far less. If the chlorohydrate could be made from bauxite, it could possibly be made at a lower cost than aluminum sulfate.

The purpose of this research was to make an in-depth investigation into phosphorus removal by aluminum chlorohydrate. Specific objectives were: (1) to compare phosphate removal of aluminum chlorohydrate and aluminum sulfate, (2) to determine a possible mechanism by which aluminum chlorohydrate removes phosphate, and (3) to study possible modes of synthesis.

LITERATURE REVIEW

Examination of the literature shows some contradictory opinions over the mechanism of removal of phosphate by the aluminum ion. Lea, Rohlich et al.[5] propose an adsorption mechanism. The preponderance of recent work points to a precipitation mechanism. Henriksen[6] and Farrell, Salotto et al.[7] believe there is a stoichiometric ratio between aluminum added and phosphorus removed. Leckie and Stumm[8] state that a precipitate of $AlPO_4 \cdot 2H_2O$ (Variscite) is formed. This precipitate is colloidal and must be coagulated with an excess of the aluminum ion.

Hsu and Bates[9] have investigated the structure of hydroxy-aluminum polymers in water solution. These polymers exist when the OH/Al ratio is 2 or greater. They propose that the polymers are composed of two planes of hydroxyl ions arranged in a close-packed order. Al^{+3} resides in the octahedral holes between the planes. Al^{+3} ions are distributed as multiples of six-member rings. The coordination number 6 of the Al^{+3} ions at the edge are not satisfied by OH^- ions but by water molecules. Figure 1 shows various forms of these polymers with OH/Al ratios of 2 and above. The average positive charge per aluminum atom is seen to decrease with increasing OH/Al ratio and polymer size.

Hsu[10] has prepared hydroxy-aluminum polymers with OH/Al ratios greater than 2 and investigated the manner in which they are precipitated by phosphate ($H_2PO_4^-$). These polymers were prepared by adding NaOH to $AlCl_3$ solution, so they were essentially chlorohydrates of "basicity" greater than 67%. (Basicity is used as defined by the British authors.[4] Hsu has a different definition which is not used here.) No precipitation occurred until the isoelectric point, defined as the point where the sum of $H_2PO_4^-$ and OH^- equals Al^{+3} on an equivalent basis. Then further addition of $H_2PO_4^-$ precipitated the aluminum completely and immediately. The precipitates contained a relatively high P/Al ratio. For example, a polymer with an OH/Al ratio of 2.55 produced a precipitate with a P/Al ratio of 0.45. Following Hsu's reasoning, a polymer with an OH/Al ratio of 2.0 would produce a precipitate with a P/Al ratio of 1.

EXPERIMENTAL PROCEDURE

Studies of phosphate removal were conducted in batch-type "jar test" laboratory experiments. For each test, one liter of synthetic effluent or actual secondary effluent was placed in a 1500 ml beaker. Twelve tests were performed at a time, using two six-position Phipps-Bird Multiple Stirring Units, one for the aluminum chlorohydrate testing and the other for aluminum sulfate tests. Appropriate amounts of aluminum compounds, acids, or bases were added at the same time to establish pH and aluminum to phosphorus molar ratios. Final pH was measured in the unfiltered supernatant. Mixtures were stirred for two minutes at 100 rpm, flocculated for five minutes at 20 rpm, and settled for one half hour.[7] Aluminum and phosphorus content of the filtered supernatant and the precipitate were determined by atomic absorption and by standard methods.[11] Synthetic

effluent containing pure orthophosphate (Table 1) and an effluent from a conventional secondary treatment plant were used for the phosphate removal studies. Composition of the synthetic effluent was the same as that used by Farrell, Salotto et al.[7] The effluent from the secondary plant was similar to the Lebanon effluent described by these authors. All experiments were conducted at ambient temperature (25° C). The pH values were adjusted with HCl or NaOH in the range values 4 to 9.

RESULTS

Before phosphorus removal studies with aluminum chlorohydrate could be initiated, the compound had to be purchased or synthesized. Synthesis of aluminum chlorohydrate from aluminum hydrate and hydrochloric acid was attempted according to the Equations 1 and 2. The results of synthesis by those methods using alumina hydrate as the raw material were inconclusive. The alumina hydrate ($Al_2O_3 \cdot 3H_2O$) appeared to be inert to all forms of acid reaction including dispersion attempts using procedures described by Hughes.[12] The attempt to make aluminum chlorohydrate from alumina hydrate was terminated when the sample of commercially prepared aluminum chlorohydrate was received from Great Britain. An analysis was performed on this compound to determine its properties. The methods of production were not released, and very little information was given out concerning the properties of this compound. Chemical analyses of the commercial product are presented in Table 2.

Table 1

Synthetic Secondary Effluent
Characteristics of Average Secondary Effluent

Elements	mg/l
Aluminum	0.1
Calcium	65.9
Magnesium	18.1
Sodium	117.7
Potassium	14.2
Sulfate	168.8
Bicarbonate	185.0
Total Phosphorus	8.05
Chloride	143.1

Table 2

Element	% Composition (Dry Basis)	Millimoles per gram
Aluminum	15.70	6.00
Iron	0.77	0.08
Calcium	0.89	0.08
Magnesium	0.46	0.20
Sodium	0.90	0.40
Potassium	0.32	0.08
Sulfate	0.38	0.04
Chloride	29.90	8.00
Phosphorus	Nil	Nil
Zinc	0.38	0.06

From the data in Table 2, this sample of aluminum chlorohydrate may be represented by the empirical formula, $Al(OH)_{1.67}Cl_{1.33}$. Its "basicity" is about 56 percent.

Simultaneous jar tests were carried out in which phosphate was removed from a synthetic secondary effluent, using this commercial grade aluminum chlorohydrate in one case and aluminum sulfate in the other. Conditions, such as phosphorus level of the effluent, temperature, and the mixing and settling procedure, were nearly identical. Results are shown in Figure 2, where the phosphorus removed is plotted against pH. In the pH range from 4 to 8, the aluminum sulfate is seen to be far more effective at removing phosphate. For example, at pH of 6.0 and the molar dose level of 1.7-1.8 Al/P, aluminum sulfate removed 96% of the phosphate whereas aluminum chlorohydrate removed about 50%.

At pH values above 8, there is an increase in removal which seems higher for the aluminum chlorohydrate than for the aluminum sulfate. The tabulated data in Tables 3 and 4 show that this is related to the appearance of calcium in the precipitate. This phenomenon has not been fully investigated so no further comment is warranted.

The markedly poor performance of aluminum chlorohydrate relative to aluminum sulfate was further substantiated by tests performed with secondary effluent from a local treatment plant. The phosphate removals obtained with the aluminum chlorohydrate are compared with removals obtained with aluminum sulfate by Farrell, Salotto et al.[7] with effluent from this plant, but at a lower Al/P ratio. The aluminum sulfate is seen from Figure 3 to be considerably more effective.

Since the data from all the tests performed with aluminum chlorohydrate showed that efficient phosphorus removal was not possible with this compound in its present form, it was theorized that an hydroxy-aluminum polymer was present which must be broken down to allow the aluminum reactivity to increase. Therefore, the sample of the aluminum chlorohydrate was acidified with concentrated hydrochloric acid in stoichiometric proportions to convert it to aluminum chloride. A comparison between the hydrochloric-acid-treated chlorohydrate and the chlorohydrate without hydrochloric acid addition, seen in Figure 4, shows that the percent phosphorus removal for the acid-treated material was very high (98%) at a pH of 6.5 and gradually decreased as the pH increased. This trend of removal was very similar to that observed with aluminum sulfate in all cases.

Table 3

Treatment of Synthetic Effluent with Aluminum Chlorohydrate
mg/l

Sample		pH	Aluminum Filtrate	Aluminum Prec.	P-Total Filtrate	P-Total Prec.	Calcium Filtrate	Calcium Prec.
Al/P Molar Ratio = 1.68								
Control	0	6.9	0.1		7.9		65	
	1	5.7	0.1	11.0	3.7	4.1	65	1.0
	2	6.5	0.1	11.0	3.8	4.0	65	1.0
	3	7.3	0.2	11.5	3.8	4.0	63	1.0
	4	7.7	0.3	10.5	3.8	3.9	60	7.0
	5	8.5	1.1	10.0	1.7	5.4	49	15.0
Al/P Molar Ratio = 2.35								
Control	0	6.9	0.1		7.9		61	
	1	5.1	0.3	21.5	1.4	6.8	61	1.0
	2	6.5	0.1	15.5	2.6	4.4	62	1.0
	3	7.5	0.1	15.5	2.9	5.0	60	4.0
	4	8.3	0.5	14.0	3.0	4.3	56	7.0
	5	9.1	1.5	12.5	1.2	6.6	46	21.0

Table 4

Treatment of Synthetic Effluent with Aluminum Sulfate
mg/l

Sample		pH	Filtrate Aluminum	Filtrate P-Total	Filtrate Calcium
Al/P Molar Ratio = 1.3					
Control	0	6.9	0.1	7.9	62
	1	4.2	1.4	1.1	63
	2	6.0	0.1	0.8	61
	3	7.0	0.1	1.5	58
	4	8.0	0.3	2.3	56
	5	9.0	1.9	2.0	48
Al/P Molar Ratio = 1.8					
Control	0	6.9	0.1	7.9	59
	1	5.0	0.1	0.1	61
	2	6.0	0.1	0.3	60
	3	6.7	0.1	0.4	60
	4	7.8	0.3	1.0	54
	5	8.9	2.0	1.8	52

The low removal of phosphate could possibly be attributed to poor quality of the commercial grade of aluminum chlorohydrate. Consequently, aluminum chlorohydrate was synthesized and evaluated for phosphorus removal under the conditions at which the commercial product was evaluated. This chlorohydrate was prepared by combining reagent-grade aluminum chloride and sodium hydroxide in the stoichiometric proportions to give the chlorohydrate, $Al_2(OH)_4Cl_2$, as a solution containing 10 mg of aluminum per ml. The phosphorus removal tests showed that the laboratory-prepared aluminum chlorohydrate performed in the same fashion as the commercial product. The highest phosphorus removal was 83% for an aluminum-to-phosphorus molar ratio of 2.9.

The poor phosphorus removal results with the aluminum chlorohydrate made it unprofitable to continue experiments to see if it could be synthesized from low cost materials such as bauxite. Screening tests were run with this chemical, aluminum sulfate, and others to evaluate their performance as conditioning aids for dewatering waste activated sludge. In these tests, the commercial grade of aluminum chlorohydrate perfbrmed better than aluminum sulfate, based on the added aluminum ion dose.

DISCUSSION AND CONCLUSIONS

The experimental results have conclusively demonstrated that the commercial grade of aluminum chlorohydrate is much inferior to aluminum sulfate for phosphorus removal from wastewater in the pH range of 4 to 8. Addition of hydrochloric acid to convert the chlorohydrate to aluminum chloride brought its performance up to the same level as the aluminum sulfate.

The poor phosphorus removal obtained with the commercial product was duplicated with aluminum chlorohydrate prepared as a solution from reagent-grade chemicals. The poorer phosphate removal can thus be attributed to the nature of the chemical rather than to its source or a particular method of manufacture.

Some insight into the difference in phosphorus removal abilities of aluminum sulfate and aluminum chlorchydrate can be obtained by considering addition of aluminum sulfate to wastewater. Concentrated aluminum sulfate solution is dispersed in wastewater at the high dilutions used to remove phosphate (e.g., Al concentration of 20 mg/l). The mixed solution is at a relatively high pH, typically from pH 5 to 8, and there is an excess of OH^- ions. Polymeric hydroxy-aluminum ions tend to form. There is apparently a competition between hydroxyl and phosphate for the aluminum. For example, in the absence of rapid mixing, phosphorus removal will be inefficient. The aluminum salt may have gone all the way to a polymeric form without contacting phosphate.

Aluminum chlorohydrate solution may be considered as "pre-reacted." It is already in a form in combination with hydroxyl ions. The situation is analogous to aluminum sulfate addition with poor mixing. Progress to formation of polymeric hydroxy-aluminum ions has obviously proceeded far enough to make it difficult for phosphate to contact aluminum ions. No predictions can be made from these results as to the nature of the intermediate structure present in aluminum chlorohydrate but the data are consistent with the proposals that hydroxy-aluminum structures do exist and that they shield phosphate from reaction with the aluminum ion.

The relatively high ratio of phosphate to aluminum in the precipitates obtained by Hsu are not at variance with the results of this study. Hsu supplied only phosphate to the hydroxyl-aluminum polymers which were at a pH too low to precipitate. In the present study, when the chlorohydrate was diluted with wastewater, it was simultaneously exposed to phosphate and to sufficient hydroxyl to precipitate it. Under these circumstances, the relative rates of reaction enter, and phosphate removal is lower than might be anticipated.

It is interesting that aluminum chlorohydrate is more effective than aluminum sulfate for conditioning wastewater sludges. It is evident that the intermediate structure present in the chlorohydrate is not a factor in its ability to condition sludge.

Until additional uses for aluminum chlorohydrate are developed, it is unlikely that enough of a market will develop to warrant its production in this country. A limited amount of work is planned to find out the effectiveness of this chemical for removing phosphate in the pH range near 9.

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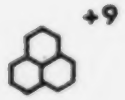
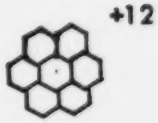
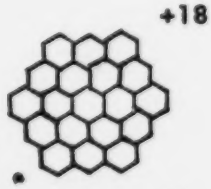


Formula	$[Al_6(OH)_{12}]^{+6}.12H_2O$	$[Al_{13}(OH)_{30}]^{+9}.18H_2O$
Charge/Al atom	+1	+0.7





Formula	$[Al_{24}(OH)_{60}]^{+12}.24H_2O$	$[Al_{54}(OH)_{144}]^{+18}.36H_2O$
Charge/Al atom	+0.5	+0.33

Figure 1. POSSIBLE FORMS OF ALUMINUM-HYDROXYL POLYIONS AND AVAILABLE CHARGE ASSOCIATED WITH THEM

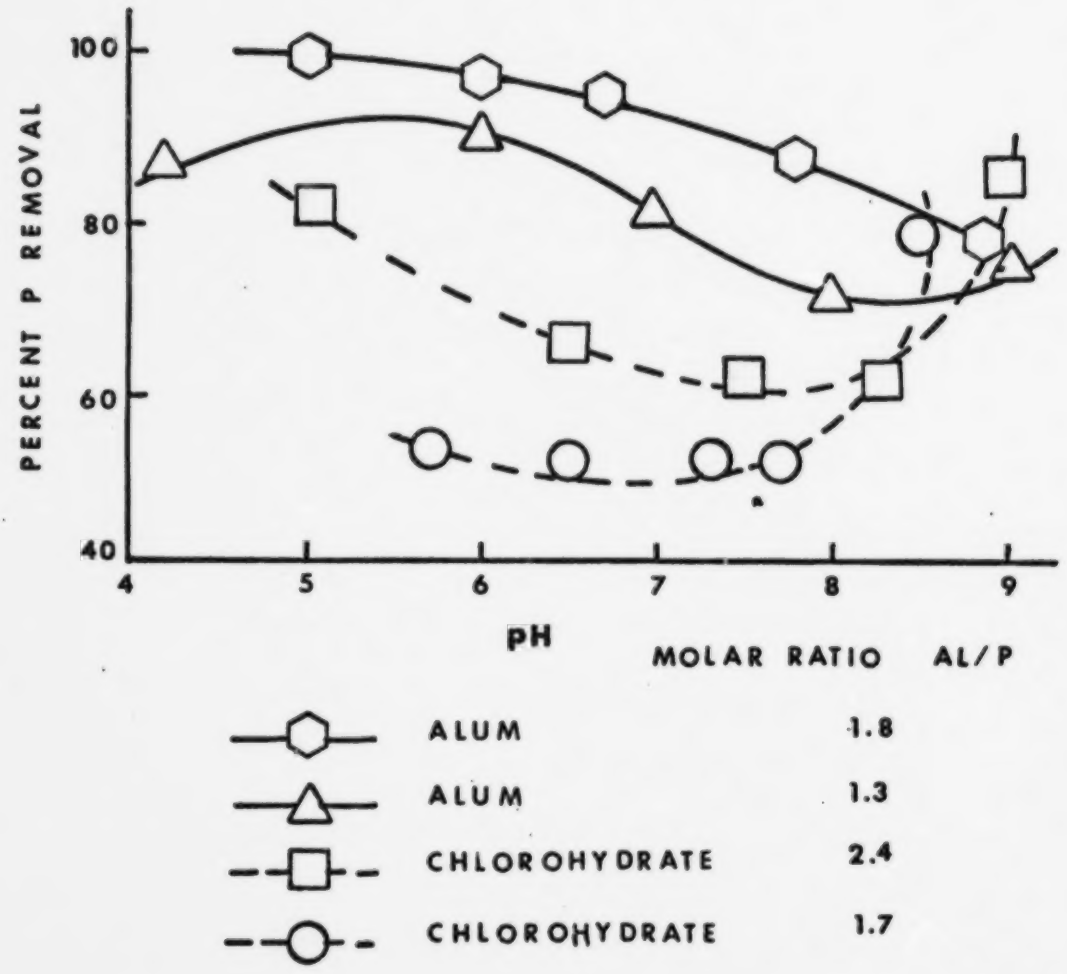


FIGURE 2. PHOSPHORUS REMOVAL COMPARISON BETWEEN ALUMINUM CHLOROHYDRATE AND ALUMINUM SULFATE-SYNTHETIC EFF.

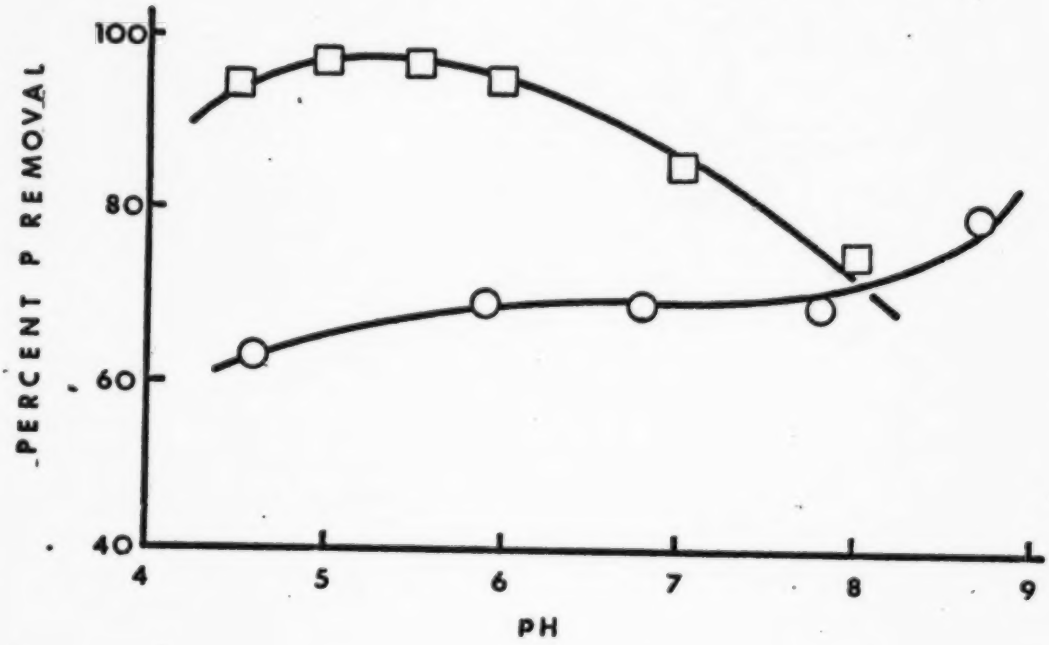
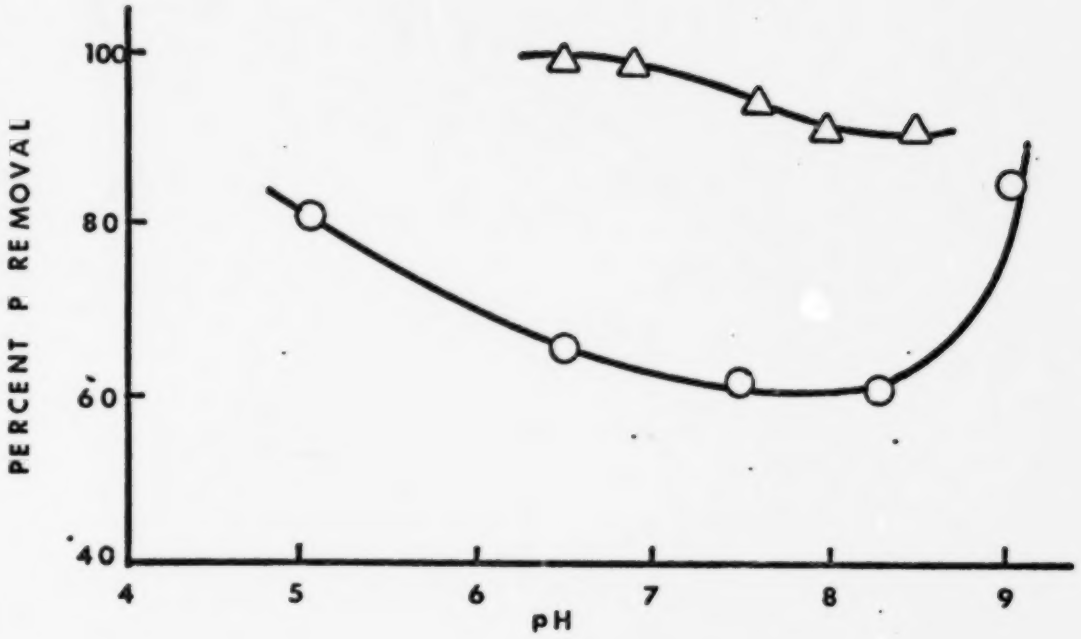


FIGURE 3. COMPARISON OF PHOSPHORUS REMOVAL BETWEEN ALUMINUM SULFATE AND ALUMINUM CHLOROHYDRATE IN ACTUAL SECONDARY EFFLUENT



MOLAR RATIO AL/P

△ ACID TREATED CHLOROHYDRATE 2.5

○ CHLOROHYDRATE 2.4

FIGURE 4. EFFECT OF HCl ADDITION TO ALUMINUM CHLOROHYDRATE ON PHOSPHORUS REMOVAL - SYNTHETIC EFF.